

**IMPROVEMENT IN OXYGEN
DELIGNIFICATION OF OIL PALM EMPTY
FRUIT BUNCHES (EFB) SODA-AQ PULP AND
USE OF EXPERIMENTAL DESIGN FOR
PROCESS OPTIMISATION**

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UNIVERSITI SAINS MALAYSIA

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PROCESS OPTIMISATION**

By

NG SOO HUEY

**Thesis submitted in fulfilment of the requirements for the
Degree of Master of Science**

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LIST OF ABBREVIATIONS AND SYMBOLS

Absorbable Organic halogen	AOX
About	\pm
Active alkali	AA
Alkaline charge	A_c
Alkaline extraction	E stage
Alkaline Peroxide Mechanical Pulping	APMP
alpha	α
Analysis of Variance	ANOVA
Anno Domini	A. D.
Anthrahydroquinone	AHQ
Anthraquinone	AQ
asterisk	*
Before Christ	B. C.
Bengal rose	BR
beta	β
centipoise	cP
Central Composite Design	CCD
Chelation	Q stage
Chemimechanical pulping	CMP
Chemithermomechanical pulping	CTMP
Chlorination	C stage
Chlorine	Cl_2
Chlorine dioxide	D stage
Chlorine dioxide	ClO_2
Cobalt ion	Co^{2+}

Coefficient Estimation	CE
Copper ion	Cu^{2+}
cubic centimetre per gram	cm^3/g
Cupriethylenediamine	CED
degree Celsius	$^{\circ}\text{C}$
degree of polymerisation	DP
Delta	Δ
Diethylenetriaminepentaacetic acid	DTPA
Diethylenetriamine-penta-methylene phosphonic acid	DTPMPA
Diphenylmethane	DPM
Electron	e^-
Elementary chlorine free	ECF
Empty fruit bunch	EFB
Equals	=
Equation	Eq.
Etcetera	etc.
Ethylendiaminepentaacetic acid	EDTA
Ferum ion	Fe^{2+}
Fresh fruit bunches	FFB
Galacan-lignin compound	Gal-L
Galactomannan	guar gum
Glucomannan-lignin compound	GlcMan-L
Grammage	g/m^2
Half fraction two-level factorial designs	2^{k-1}
Heptamolybdopentavanadophosphate heteropolyaion	$[\text{PMo}_7\text{V}_5\text{O}_{40}]^{8-}$ (HPA-5)
Heteropolyacids	HPAs
Hexenuronic acid	HexA

High level	(+)
Hydrogen peroxide	H ₂ O ₂
Hydrogen peroxide bleaching	P stage
Hydrogen peroxide reinforced O stage	O _P stage
Hydroperoxide anion	HOO ⁻
Hydroperoxy radical	HOO [·]
Hydroxyl radical	HO [·]
Hypochlorite	H stage
Impregnation, Delignification and Extraction pulping	IDE
International Organisation for Standardization	ISO
Kappa number	K _n
Kilopascal	kPa
Lack of Fit	LOF
Lignin-carbohydrate complexes	LCC
Litre	L
Low level	(-)
Manganese ion	Mn ²⁺
Magnesium sulfate	MgSO ₄
mega Pascal	MPa
Meso(tetrasulfonatophenyl) porphyrin	TSPP
Meter	m
Methylene blue	MB
Millilitre	mL
Millimetre	mm
mililitre pre gram	mL/g, mLg ⁻¹
mili pascal second	mPa.s
Mn(II)-substituted heptamolybdopenta- vanadophosphate heteropolyaion	HPA-5-Mn ^{II}

Model Summary Statistic	MSS
Molarity	M
Newton	N
Nitrogen oxide	NO _x
Normality	N
Old corrugated container	OCC
Organic radicals	R [•] , RO ₂ [•]
oven dry	o.d.
Oxy ion	O ⁻
Oxygen	O ₂
Oxygen alkaline extraction	(EO) stage
Oxygen delignification	O stage
Ozone	O ₃
Ozone delignification	Z stage
Ozonide anion radical	O ₃ ^{-•}
percentage	%
percentage of AQ	A _q
Peroxide anion	O ₂ ²⁻
Peroxyacetic acid or Peracetic acid	Paa
Peroxymonosulphuric acid	Ps
Polyoxometalates	POMs
Potassium hydrogen phthalate	KHP
Potassium hydroxide	KOH
Potassium iodate	KIO ₃
Potassium iodide	KI
Potassium permanganate	KMnO ₄
pounds-force/sq.inch	psi

Predicted Residual Sum of Squares	PRESS
Prehydrolysed, Impregnation, Delignification and Extraction pulping	HIDE
Reaction temperature	T
Reaction time	t
Redox potential	E^0
Reducing end group	REG
Response Surface Methodology	RSM
round per minute	r.p.m.
R-squared	R^2
Sendirian Berhad	Sdn Bhd
Sequential Model Sum of Squares	SMSS
Singlet oxygen	$^1O_2^*$
Sodium hydroxide	NaOH
Sodium hypochlorite	NaOCl
Sodium oxalate	$Na_2C_2O_4$
Sodium thiosulfate	$Na_2S_2O_3 \cdot 5H_2O$
Sulphuric acid	H_2SO_4
Superoxide anion radical	$O_2^{\cdot -}$
Technical Association of Pulp and Paper Industry	TAPPI
Tetrasulfophthalocyanine	TSPc
Thermomechanical Pulping	TMP
three dimensional	3D
totally chlorine free	TCF
tonnes per hectares	ton/hect
Triplet state Oxygen	3O_2
Two stages of O stage	OO stage
Two-level Factorial Design	2^k

Ultraviolet	UV
Volt	V
Water	H ₂ O
OO stage with interstage washing	O/O stage
OO stage without interstage washing	O-O
Xylan-lignin Compound	Xy-L

**PEMBAIKAN DELIGNIFIKASI OKSIGEN BAGI PULPA SODA-AQ TANDAN
KOSONG KELAPA SAWIT DAN PENGGUNAAN REKA BENTUK UJIKAJI
UNTUK PENGOPTIMAAAN PROSES**

ABSTRAK

Delignifikasi bagi pulpa soda-AQ tandan kosong kelapa sawit (*Elaeis guineensis*) dengan oksigen dihadkan pada 38% demi mengelakkan degradasi selulosa yang serius. Untuk meningkatkan keberkesanan bagi delignifikasi oksigen (peringkat O), sejumlah kecil hidrogen peroksida (H_2O_2) bersama atau tanpa antrakuinone (AQ) ditambahkan semasa oxygen delignifikasi dan dikenali sebagai delignifikasi oksigen diperkuat dengan hidrogen peroksida (peringkat O_p), manakala dengan penambahan AQ dikenali sebagai peringkat O_p dengan pembantuan-AQ. Pada kajian awal, delignifikasi oksigen dengan penambahan H_2O_2 dan AQ telah menunjukkan potensi untuk meningkatkan penurunan nombor kappa (K_n) dan kecerahan pulpa. Maka kesan interaksi bagi H_2O_2 dan AQ bersama dengan tiga faktor proses iaitu suhu tindak balas ($^{\circ}C$), masa tindak balas (t), dan kepekatan alkali (A_c) pada oksigen delignifikasi bagi pulpa hasilan tandan kosong kelapa sawit dikaji secara statistik dengan menggunakan rekabentuk ujikaji dua-tingkat pemfaktoran separuh (2^{k-1}) supaya menyingkirkan faktor yang tidak signifikan. Berdasarkan model-model faktor yang dibina, H_2O_2 (P), suhu tindak balas (T) dan kepekatan alkali (A_c) memberi kesan yang signifikan kepada semua sifat. Di samping itu, kemerosotan kelikatan pulpa dengan kandungan H_2O_2 yang tinggi dapat dikurangkan secara signifikan dengan penambahan AQ dalam kuantiti yang sedikit. Tambahan lagi, semua model faktor yang dibina adalah sah secara statistik dan eksperimen. Pengoptimuman peringkat O_p dengan pembantuan-AQ dilakukan dengan rekabentuk ujikaji Metodologi Permukaan Sambutan (response surface methodology, RSM) berdasarkan rekabentuk komposit pusat (central composite design, CCD) dengan tiga faktor individu iaitu $H_2O_2^*$ (P^* , 0.25-2.00%), suhu tindak balas (T^* , 70-110 $^{\circ}C$), dan kepekatan alkali (A_c^* , 1.2-2.8%) serta faktor tetap iaitu 30 min masa tindak balas dan 0.02% AQ.

Analysis rekabentuk komposit pusat mendapati A_c^* adalah tidak signifikan bagi sifat kelikatan selulosa, tetapi kepekatan A_c^* yang tidak mencukupi akan menyebabkan kemerosotan kelikatan selulosa juga terutamanya dalam keadaan P^* dan T^* yang tinggi. Keadaan optimum kiraan bagi peringkat O_p dengan pembantuan-AQ adalah 1.4% H_2O_2 dan 2.4% NaOH, pada 100 °C dan K_n , kelikatan selulosa dan kecerahan bagi pulpa yang terhasil masing-masing adalah 6.5, 12.4 cP dan 61.92% (ISO), dan kesemua nilai adalah tidak berbeza secara signifikan dengan nilai yang dikira. Rawatan cahaya dengan lampu biru (400-500 nm) sebelum peringkat O menunjukkan potensi bagi meningkatkan pemilihan peringkat O.

**IMPROVEMENT IN OXYGEN DELIGNIFICATION OF OIL PALM EMPETY
FRUIT BUNCHES (EFB) SODA-AQ PULP AND USE OF EXPERIMENTAL
DESIGN FOR PROCESS OF OPTIMISATION**

ABSTRACT

The delignification of oil palm (*Elaeis guineensis*) empty fruit bunch fibres soda-AQ pulp by oxygen is limited to 38%, to avoid substantial cellulose degradation. To enhance the effectiveness of oxygen delignification (O stage), small amounts of hydrogen peroxide (H_2O_2) with and without anthraquinone (AQ) are added during oxygen delignification, which are known as the hydrogen peroxide reinforced oxygen delignification (O_p stage) and AQ-aided O_p stage respectively. The preliminary study of the addition of hydrogen peroxide and anthraquinone (AQ) to oxygen delignification has shown their potential on improving kappa number (K_n) reduction and pulp brightness. Hence, the interaction effects of hydrogen peroxide and anthraquinone, and the other three process variables viz. reaction temperature (T), reaction time (t) and alkaline charge (A_c) on oxygen delignification of pulp produced from oil palm (*Elaeis guineensis*) empty fruit bunch fibre are statistically investigated by employing a half two-level factorial (2^{k-1}) experimental design in order to screen out the insignificant effects. Based on the factorial models built, H_2O_2 (P), reaction temperature (T) and alkali charge (A_c) are significant to all of the responses. Besides, the impairment to the pulp viscosity by a relatively higher level of H_2O_2 (2.0% on the oven-dry weight of pulp) is found to be significantly countered by adding a small amount of anthraquinone. Furthermore, all factorial models built are also statistically and experimentally validated. The optimisation of the AQ-aided O_p stage is operated with response surface methodology (RSM) through central composite design (CCD) with three independent variables namely $H_2O_2^*$ (P^* , 0.25-2.00%), reaction temperature* (T^* , 70-110 °C), and alkali charge* (A_c^* , 1.2-2.8%) and the fixed variables are 30 min reaction time and 0.02 % AQ. The analyses of CCD found that A_c^* gives an insignificant effect to the pulp viscosity, which however an insufficient of A_c^*

causes a serious decrease of the pulp viscosity especially when the P^* and T^* are in high level. The calculated optimum condition for AQ-aided O_P stage is 1.4% H_2O_2 with 2.4% NaOH at 100 °C and the K_n , pulp viscosity and brightness of the resultant pulp are 6.5, 12.4 cP and 61.92% (ISO) respectively, which are significantly no different from the calculated values. A photo-treatment by using blue light (400-500 nm) prior to the O stage also shows potential to improve the O stage selectivity.

CHAPTER 1 INTRODUCTION

1.1 General

Since the 1980s, it had been reported that highly toxic and environmental persistent polychlorinated dioxins and furans were detected in the effluent of bleaching plant (Nelson, 1998). Thus, the new approach of bleaching technologies like elementary chlorine free (ECF) and totally chlorine free (TCF) bleaching were introduced with the aim to reduce the highly toxic chlorinated compounds in the effluent. Soon after, many works had been carried out extensively on investigating and examining the performance of ECF and TCF bleaching towards different kinds of pulps (Reeve and Weishar, 1991; McDonough, 1995; Leroy et al., 2004).

It is a well-established fact that in order to achieve the highest efficacy of TCF bleaching; the capability of delignification in first bleaching stage is most important (Sippola and Krause, 2005; Agarwal et al., 1999). Amongst the chlorine-free bleaching stages, oxygen delignification (O stage) has shown its potential during the first stage of TCF bleaching, since it is capable to remove the residual lignin in the pulp up to 50% without significant detrimental effect on the pulp strength. In addition, Beyer and co-workers implied that bleaching with ozone causes strong yellowing while oxygen will not (Beyer et al., 1999). However, if compared with the conventional chlorination (C stage) and chlorine dioxide (D stage), O stage shows lower effectiveness since the further elimination of lignin will cause serious degradation of the carbohydrates (Parthasarathy et al., 1990; Leroy et al., 2004)

Amongst the studies, some reported that the addition of hydrogen peroxide (H_2O_2) in O stage had improved the delignification and had retained the pulp viscosity at an acceptable level on softwood kraft pulp (Farley, 1973; Parthasarathy et al., 1990; Boman et al., 1995). Parthasarathy et al. (1990) have reported that small amount of H_2O_2 (less than 0.5% on oven dry (o.d.) pulp) should be added since the further increase of H_2O_2 charges would lower the

viscosity as compared to the conventional O stage. Nevertheless, the results of the study showed that the pulp brightness only gained little benefits with the addition of small amount of H_2O_2 . Furthermore, unenviable decomposition of H_2O_2 to very reactive radicals would occur when high temperature and alkaline were employed during O stage. This would cause carbohydrate degradation with the presence of transition metals.

By controlling the decomposition of H_2O_2 , in cooperation with a pre-treatment—a combination of nitrosation and metal chelation, higher charge of H_2O_2 (1.0% on o.d. pulp) could be employed during the H_2O_2 reinforced O stage (O_P stage) to remove up 65% of the residual lignin and retained substantially high viscosity of the softwood kraft pulp (Stevens and Hsieh, 1995). Moreover, Argyropoulos et al. (2003, 2004) had endeavoured that borax and 1,10-phenanthroline in O_P stage would give a promising result to preserve viscosity and concomitantly would increase the rate of delignification and ISO brightness on softwood kraft pulp. However, attempts to improve O stage on lignocellulosic materials other than softwood have yet to be carried out. The authors also stated that the addition of 0.3% 1,10-phenanthroline may cause an increase of about 30% in the NO_x discharge from the recovery boiler.

Besides, photo treatment prior to O stage had also shown its potential to improve or extend the oxygen delignification. A number of researches reported that when lignocellulosic materials absorb ultraviolet (UV) and visible light, they will generate active species, and thus cause photodegradation of lignocellulosic materials (Krinhstad, 1969; Schmidt et al., 1990; Davidson, 1996, Bikova and Treimanis, 2004). Sun et al. (1996) showed that an involvement of UV-peroxide stage in TCF bleaching successfully bleached the radiate pine kraft pulp up to 90% ISO of brightness. Besides, Da Silva Perez et al. (2002) also proved that photodegradation had occurred in *Eucalyptus grandis* peroxyformic/formic acid chemical pulp under irradiation of light with wavelength above 300 nm. A recent study by Ruggiero et

al. (2005) agreed that the sugar cane bagasse acidolysis lignin could be degraded via UV light.

On the other hand, oil palm *Elaeis guineensis* is one of the important crops in Malaysia since 1917 (Mohamad et al., 1986; Khor et al., 2009). In the production of palm oil, some by-products are generated such as mesocarp fibre, shell and empty fruit bunch (EFB) which is valuable to biomass resources for generating energy (Ma et al., 1994). Nevertheless, it has been recognised that the incineration of EFB causes some environmental problems (Lim and Zaharah, 2000; Tanaka, 2004; Anderson, 2008; Frank et al., 2008). Therefore, EFB is normally used for production of fibre based products such as composite and pulp for paper production.

The utilisation of oil palm biomass especially EFB in the production of pulp and paper has been introduced since the late of 1970s (Khoo and Lee, 1991). Since that, the effect of different pulping agents such as sodium carbonate, kraft, kraft-AQ, soda, soda-AQ on EFB pulping have been investigated by several groups of researchers. According to Tanaka et al. (1999) the bleachability of EFB kraft-AQ pulp is comparable with commercial hardwood kraft pulp. However, in the later studies showed that soda-AQ pulp, which is sulphur-free pulp exhibits better bleachability than kraft-AQ pulp (Leh et al., 2004; Leh et al., 2005).

Based on Leh et al. (2005), in order to achieve the ISO brightness of above 80%, TCF bleaching sequence containing ozone (Z stage) is a necessity. However, Z stage requires very high investment costs for the ozone generator and its auxiliary equipments and also rather high operating cost due to high power consumption. Hence, one way to consider the establishment of a small scale pulp mill which uses EFB as raw material, a simple TCF bleaching sequence without Z stage should be recommended. Therefore, an imperative action to improve O stage becomes a necessity.

Aforementioned, O_p stage is a preferable attempt to improve oxygen delignification. However, without the employment of any pre-treatment such as nitrosation or metal chelation (Stevens and Hsieh, 1995), substantial losses of pulp viscosity is inevitable. In order to minimise the cellulose deterioration in an O_p stage towards oil palm EFB soda-anthraquinone pulp, an attempt has been made by adding anthraquinone (AQ) to the system in this study. Consequently, a half two-level factorial design has been used to analyse the effect of five bleaching variables—the H_2O_2 charge (P, %), reaction temperature (T, °C), reaction time (t, min), alkali charge (NaOH, %), and percent of AQ (A_q , %) on three properties of the pulp which are the kappa number (K_n), pulp viscosity (cP) and brightness (ISO). According to the variables selected in two-level factorial designs, response surface methodology (RSM) via a central composite design (CCD) has been applied to optimise the H_2O_2 reinforced oxygen delignification.

In addition, due to the natural ability light absorber of lignocellulosic materials, photo pre-treatment brings an ancillary approach to improve oxygen delignification. Consequently, a photo pre-treatment by using blue light in visible spectrum range (400-500 nm) has also been carried out on EFB pulp in this study.

Delignification of EFB soda-AQ pulp by oxygen has been limited to only 36.72% which substantially limits its role in the bleaching process (Koay, 2008). This research focuses on improving the selectivity of oxygen delignification using a hydrogen peroxide (H_2O_2) reinforced O stage (O_p stage) via addition of anthraquinone (AQ) and photo pre-treatment of the pulp using blue light in visible spectrum range (400-500nm).

1.2 Objectives

This research was carried out in order to improve of oxygen delignification on EFB soda-AQ pulp. Objectives of this research are as below:

- To improve the selectivity of oxygen delignification on EFB soda-AQ pulp by addition of hydrogen peroxide (H_2O_2) with and/or without anthraquinone (AQ).
- To statistically identify the combined effect of AQ-aided hydrogen peroxide reinforced oxygen delignification.
- To optimise the AQ-aided hydrogen peroxide reinforced oxygen delignification by employing response surface methodology (RSM).
- To investigate the effect of photo pre-treatment (in the spectrum range 400-500 nm) on the selectivity of oxygen delignification.

CHAPTER 2 LITERATURE REVIEW

2.1 An Overview of Pulp Bleaching

Generally, pulp produced from lignocellulosic materials is brownish or yellowish in colour which thereby limits its application for high quality paper products. In order to increase pulp brightness, it is necessary to bleach the pulp. Through a bleaching process, pulp brightness can be increased by either eliminating the lignin or only altering the chromophoric structures to non-chromophoric structures without eliminating the lignin (brightening). The application of these two bleaching custom is dependent on the preceding pulping method. Basically, bleaching by eliminating lignin will be applied on chemical pulp, while high yield pulp such as mechanical and semimechanical pulp will be bleached by only changing the chromophoric structures in the lignin.

Since the lignin still remain in the bleached high yield pulp, the chromophoric structures can be generated back through oxidation with the presence of oxygen and light and causing colour reversion – yellowing the bleached pulp. This indicates a low brightness stabilizing of high yield pulp. In order to obtain bleached pulp with high brightness stability pulp, chemical full bleached pulp is preferred. On the other hand, high brightness pulp can hardly be achieved by using one stage bleaching only. Hence, a multistage bleaching sequence is possible to get higher pulp brightness. On the other hand, carbohydrate degradation should be controlled at a minimum level during the bleaching process in order to preserve pulp strength and paper making properties. To obtain high quality bleached chemical pulp, an appropriate bleaching sequence condition is very important for pulp bleaching (Casey, 1966; Dard, 1978; Smook 1992; Reeve, 1996).

2.1.1 Brief History and Development of Pulp Bleaching

The technique of bleaching on clothes and linen by using lime as a bleaching agent started in 300 B.C. viz more than 400 years ago prior to the invention of paper by Ts'ai Lun in A.D. 105. Consequently, in 100 A.D., white linen was also produced by scouring it with alkali followed by washing as well as exposing to the sun. However, the technique of bleaching for pulp and paper is only established in the early nineteenth century when the chemical wood pulp commenced. (Dard, 1978; Reeve, 1996).

In 1774, Karl Wilhelm Scheele (1742 - 1786) found the element of chlorine and its ability to destroy vegetable colouring compounds as discovered by C.L. Berthollet in 1784 (Dard, 1978; Sjöström, 1993). In the following year in France, Berthollet revealed that chlorine can be dissolved in the solution of vegetable ash, potash (any salts of potassium) and the name “eau de Javelle” is given (Reeve, 1996). About ten years later (in 1799), Charles Tennant of Glasgow discovered that the suspension of lime, which is cheaper than vegetable ash, can be used for pulp bleaching as the suspension can absorb chlorine gas to form calcium hypochlorite (Histed et al., 1996). Consequently, this chemical became a typical bleaching agent in the nineteenth century (Reeve, 1996).

As a matter of fact, bleaching of pulp only become more important and challenging after the industrial revolution in the early of nineteenth century, as the demand of raw material such as cotton, rag or linen of pulp for production was outstripping supply (Dard, 1978). Thus, a new raw material which should be made available in large quantity is necessary. In the 1840s, Friedrich Gottlob Keller invented a wood-grinding machine thus producing cheaper ground wood papers. Since then, raw materials for paper pulp had been replaced by wood fibres. However, the coarseness of ground wood pulp limits its application. In 1851, the first chemical wood pulp (soda process) was developed by Hugh Burgess and Charles Watt (Dard, 1978). Nevertheless, chemical wood pulp is darker and is more difficult to be bleached in comparison to non-wood fibres used previously.

In order to obtain higher brightness pulp from wood fibre, multi-stages bleaching is required. The bleaching sequence used should also appositely be according to pulp requirements. In the 1800s to the early 1900s, hypochlorite (H stage) and alkaline extraction (E stage) are the only two bleaching stages employed and the common bleaching sequence is HEH. In the 1930s, the first stage of bleaching is replaced by elemental chlorine, which is known as chlorination (C stage). C stage is relatively cheaper and attacks the lignin selectively with less carbohydrates degradation. Hence, the most common used bleaching sequence during that period of time shifts to CEH. During the same decade (1930s), Mathieson Chemical Corp. generated chlorine dioxide by adding sodium chlorite in pulp suspension and chlorine gas. However, the use of chlorine dioxide (D stage) just begins during the 1940s, when the five stages of bleaching sequence as CEDED were introduced (Reeve, 1996). The fast growth of the D stage was due to its capability to produce high brightness pulp while retaining sufficient pulp strength (Sjöström, 1993; Reeve, 1996). In the 1980s, highly toxic and environmental persistent compounds such as dioxin, furan and chlorinated organic compound are detected in the effluent discharged from pulp mills (Nelson, 1998).

Due to the pressure from environmental protection groups and also government agencies toward pulp mills, a new bleaching trend, which is more environmental friendly namely elemental chlorine free (ECF) bleaching and totally chlorine free (TCF) bleaching, is recommended. In ECF bleaching, the C stage which uses elemental chlorine as a bleaching agent is excluded in the bleaching sequence and is replaced by D stage as the first bleaching stage. Thus the bleaching sequence of DEDED is then used conventionally (Daniel et al., 2004; Leroy et al., 2004). On the other hand, TCF bleaching emphasizes on using agents that do not contain chlorine (Cl_2), including chlorine dioxide (ClO_2) and sodium hypochlorite (NaOCl) agents, such as ozone (O_3 , ozone delignification, Z stage), oxygen (O_2 , oxygen delignification, O stage) and hydrogen peroxide (H_2O_2 , hydrogen peroxide bleaching, P stage) (Reeve, 1996; Nelson, 1998). Moreover, bio-bleaching by using enzyme (Sjöström, 1993;

Farrell et. al., 1996) and photo bleaching with UV light show their high potential in chlorine free pulp bleaching (Yan et. al., 1996).

ECF bleaching is claimed to be a move towards more environmentally compatible technology since the formation of chlorinated organic compounds has been minimized (Mcdonough, 1995; Reinstaller, 2008). However, as reported by Steffes and Germgard (1995), the replacement of D stage in ECF bleaching sequence with Z stage for TCF sequence had caused the absorbable organic halogen (AOX) emission to drop from 0.4 kg/ton of pulp to zero.

On the other hand, paper strength properties of ECF bleached paper are normally higher than TCF paper. A comparison between the chlorine counterparts and oxygen based bleaching agents towards lignin and carbohydrates is shown in Table 2-1. It is obvious to see that O_3 , O_2 and H_2O_2 are comparable to Cl_2 , ClO_2 and $NaOCl$ respectively in term of reaction towards lignin. However, the oxygen based chemicals are less selective as they attack carbohydrates as well (Hosoya, 1992; Nelson, 1998).

This indicated that even though TCF shows higher environmentally compatibility than ECF, but in terms of paper strength properties such as brightness, ECF bleached paper is normally higher than TCF bleached paper. Hence, for pulp millers, higher preference is still given to ECF (Mcdonough, 1995; Leroy et al., 2004). Consequently, it has still become a challenge for the researchers to enhance TCF bleaching selectivity by further improving its delignification and minimizing the impact on cellulose deteriorating.

Table 2-1 Classification Reaction of Bleaching Agents toward Lignin and Carbohydrate (Hosoya, 1992; Nelson, 1998)

Bleaching Agent	Lignin				Carbohydrate
	Aromatic Rings	Double Bonds	Free Phenolic Groups	Carbonyl Groups	
Cl ₂	1	1	0	0	0
ClO ₂	0	1	1	0	0
NaOCl	0	0	0	1	0
O ₃	1	1	0	0	1
O ₂	0	1	1	0	1
H ₂ O ₂	0	0	0	1	1

0: no reaction with the functional groups of lignin.

1: reaction occurs with the functional groups of lignin.

2.2 Oxygen Delignification (O stage)

Oxygen delignification is an environmental feasible process since there are extremely low chlorinated compounds detected in its effluent. Effluent is recommended to be recycled in pulp mill as a closed system (McDonough, 1995; Nelson, 1998; Barroca et al., 2001). In addition, it is also capable of delignifying up to 50% of lignin residual remained in the unbleached pulp. On the other hand, oxygen is also a cost feasible bleaching agent in comparison to chlorine dioxide (Smook, 1992; Reeve, 1996; Nelson, 1998; Barroca et al., 2001). Besides, the energy required for generating oxygen is one over eight as compared to an equivalent amount of chlorine generated (McDonough, 1989). Since, O stage has been cost advantageous and has met the environmental obligation; it is apt to be used in most of the pulp bleach plants (Tench and Harper, 1987; Smook, 1992; Reeve, 1996; Nelson, 1998; Barroca et al., 2001).

2.2.1 Development of Oxygen Delignification

Oxygen is first introduced by Joy and Camphell as a bleaching agent for paper pulp in 1867. About fifty years later, in 1915, oxygen pressurised method with the addition of the alkaline earth metal hydrate was introduced by Mueller (McDonough, 1996). After that, in late 1950's, oxygen is successfully used as a bleaching agent (McDonough, 1996, Nelson, 1998). However, oxygen is still not commonly used for pulp bleaching because it attacks both lignin

and carbohydrates unselectively. In 1960s, the advancement of O stage to preserve the pulp strength properties was found by Robert and co-worker via adding magnesium salts during O stage. Consequently, the O stage first became commercialised in South Africa in 1970 (McDonough, 1996; Nelson, 1998).

Due to the increase of environmental consciousness, O stage started to be widely used. Moreover, the effects of O stage on different types of pulp are also investigated substantially right after the confirmation in 1980s that bleaching by C stage followed by an E stage causes serious environmental problem due to the generation of chlorinated organic compounds and dioxin (Nelson, 1998). In addition, chloride containing effluent from C stage is highly corrosive (Alfonsson et al., 1993; Nagarathnamma and Bajpai, 1999).

Initially, when the O stage is employed as the first stage conventional bleaching sequence, it is capable to shorten the bleaching sequence from CEDED to OCED and at the same time it improves the resultant pulp brightness while retaining the pulp properties and also lowers the toxicity in effluent (Tench and Harper, 1987). Besides, oxygen alkaline extraction ((EO) stage) is also carried out after the first bleaching stage, either as C stage or D stage. According to a comparison between C/DED and C/D(EO)D done by van Lierop et al. (1989), the latter bleaching sequence shows higher brightness and lower K_n while maintaining the viscosity for sulphite pulp. In addition, the use of (EO) stage has saved the chemical consumption in the subsequent stage and also decreases the coloured substance in the effluent.

Nevertheless, the relatively low selectivity of O stage limits its delignification at no more than 50% viz. before causing unacceptable carbohydrates degradation. Therefore, different attempts are carried out in order to improve O stage efficiency, such as introducing a pre-treatment prior to O stage, addition of catalyst (additives), two stage of O stage (O-O stage),

and hydrogen peroxide reinforce oxygen delignification (O_p stage) started from 1990s until now (Barroca et al., 2001; Suchy and Agryropoulos, 2001 and 2002).

2.2.2 Variables Affected Oxygen Delignification

During the O stage, the variables which affect the O stage efficiency are alkali charge, time, temperature, oxygen pressure and consistency of pulp. In order to get the better mechanical and optical properties of pulp with lower operation cost, effects of each variable of the O stage on pulp properties should be understood clearly (McDonough, 1983). Besides bleaching variables, initial K_n of pulp properties will also affect the efficiency of the O stage too (Agarwal, 1999; Doğan and Gürüz, 2008).

Based on a kinetic study of the O stage, the delignification is divided into two phases, which are rapid initial phase and slow final phase. Even though the sensitivity of rapid initial phase variables is low in comparison to slow final phase, but the rate of delignification and carbohydrate degradation increases concomitant with the increase of alkali charge, temperature and oxygen pressure (Olm and Teder, 1979; McDonough, 1983; Barroca et al., 2001).

The increase of alkali charge at constant pulp consistency causes the increase of both the delignification and cellulose degradation (McDonough, 1983; Nelson 1996). The concentration of alkali charge used, usually, is based on the type of pulp and the viscosity requisite for the final pulp. However, the increase of the operation temperature and/or the reaction time decreases the concentration of alkali charge required concomitantly (McDonough, 1983). In high consistency of the O stage, each 0.13% and 0.16% NaOH is requisite to decrease apiece unit of K_n for softwoods and hardwood respectively. Subsequently, more alkali is needed in medium consistency of the O stage as the

concentration of NaOH is lower compared to high consistency in the same dosage of NaOH used (McDonough, 1983).

As aforementioned, the delignification of the O stage is divided into the rapid initial phase and the slow final phase. Delignification of the rapid initial phase happened in the first 10 minutes of the process, while the reaction time for the slow final phase is dependent on the amount of alkali charge and the final K_n required (McDonough, 1983). Barroca et al. (2001) revealed that, the initial rapid phase of the O stage gives higher selectivity. On the other hand, continuing prolongs the reaction time will limit the reduction of kappa number (Olm and Teder, 1979).

As reported by many studies, operation temperature is one of the factors affecting the rate of delignification. The increase of operation temperature also increases both the delignification and carbohydrate degradation concomitant. Higher temperature is required to enhance the rate of delignification since it will improve chemical impregnation into fibre wall (McDonough 1983; Agarwal, 1997; Barroca et al., 2001).

Among the variables, the effects of oxygen pressure on pulp during the O stage are smaller compared to alkali charge and operation temperature (McDonough, 1983; Barroca et al. 2001). Nevertheless, due to oxygen being low solubility in water, oxygen pressure is necessary to impregnate the oxygen into the pulp fibres in order to accelerate both the delignification and carbohydrate degradation (Argawal et al, 1999; Doğan and Gürüz, 2008). In comparison, with the same oxygen pressure, low consistency pulp is less affected than high consistency pulp. This is mainly due to higher water layer on the surface of pulp fibres as low consistency pulp obstructs the penetration of oxygen (McDonough, 1983). However, Olm and Teder (1979) claimed that the oxygen pressure only give the effect during the initial phase of the O stage.

Mass transfer of oxygen in the O stage is well related to the consistency of pulp. As mentioned earlier, the impregnation of oxygen is low when the consistency of pulp is low. In contrast, the mixing rate between the fibres and chemical (mass transfer) is better in low consistency than high consistency pulp (McDonough, 1983). However, Agarwal et al. (1999) expelled that there is no significant discrepancy of the mass transfer of the O stage in low and medium consistencies on mixed southern hardwood pulp.

In addition, the initial K_n of unbleached pulp claimed that it may affect the efficiency of the O stage. Lignin can be classified into two lignin fragments as “stubborn lignin” and “easily remove lignin” moieties. It is stated that with high initial K_n , lignin contains greater amount of “easily removed lignin” moieties, and they are readily being removed in the rapid initial phase of the O stage, whilst, the “stubborn lignin” is removed in the slow final phase. Consequently, the removal of “stubborn lignin” is time dependence (Argawal et al, 1999; Lucia et al., 2002; Doğan and Gürüz, 2008). Lucia et al. (2002) indicated that for the softwood kraft pulp in a single O stage, the bleachability (Δ lignin concentration/ % of NaOH) of pulp with high initial K_n is higher than that with lower initial K_n . In addition, there is a limitation to decrease the K_n even with extending the operation time.

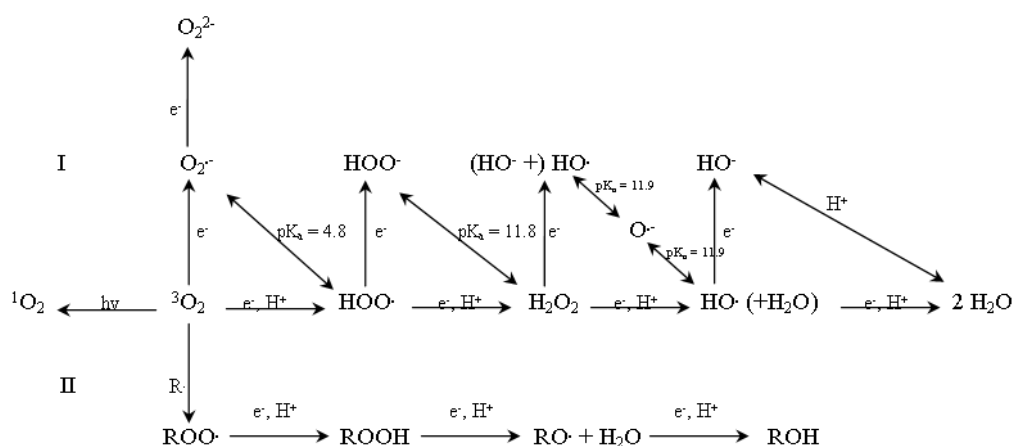
2.2.3 Chemistry of Oxygen Delignification

Oxygen, lignin and carbohydrate play the key role in the chemistry of O stage. As oxygen decomposes into different type of oxygen reactive species in O stage and the complexities of the lignin and carbohydrates structures in nature, it makes the study on the chemistry of O stage becomes more complicated. Nevertheless, by understanding the chemistry of O stage as reactions arise between oxygen reactive species, lignin and carbohydrates; it may assist to improve the O stage.

2.2.3.1 Oxygen Reactive Species in Oxygen Delignification

In O stage, oxygen reactive species which decomposed from molecular oxygen are responsible to react with the lignin and carbohydrates in the system. Molecular oxygen is a unique radical species, it contains two unpaired electrons under triplet state ($\uparrow\uparrow$, $^3\text{O}_2$), in which its non reactive species and it readily transforms it into reactive species such as superoxide anion radical ($\text{O}_2^{\cdot-}$) and singlet oxygen ($\uparrow\downarrow$, $^1\text{O}_2^*$) (Sjöström, 1993; McDonough, 1996). However, the transformation of $^3\text{O}_2$ to $^1\text{O}_2^*$ barely happens except with the presence of a catalyst and/or has been hastened by the absorption of light energy (Wasserman, 1979).

As depicted in Scheme 2-1I, $\text{O}_2^{\cdot-}$ is formed through a reduction process as $^3\text{O}_2$ accepts a single electron (e^-) in the presence of substrate such as hydrogen or ionized lignin residues. In addition, $^3\text{O}_2$ is also reduced to form hydroperoxy radical (HOO^{\cdot}), hydrogen peroxide (H_2O_2), hydroxyl radical (HO^{\cdot}) and water (H_2O) (Sjöström, 1993; McDonough, 1996; Cao et al., 2007). Furthermore, due to the fact that $\text{O}_2^{\cdot-}$ and HOO^{\cdot} have higher affinity for electrons, they tend to accept an electron to form peroxide anion (O_2^{2-}) and hydroperoxide anion (HOO^-) correspondingly. Since, HOO^{\cdot} , H_2O_2 , and HO^{\cdot} are weak acid, therefore an equilibrium amount of their anions are present as $\text{O}_2^{\cdot-}$, hydroperoxide anion (HOO^-) and oxy ion (O^-) respectively under an alkaline medium (Sjöström, 1993; McDonough, 1996; Guay et al., 1999). Furthermore, ozonide anion radicals ($\text{O}_3^{\cdot-}$) is formed through the reaction between $\text{O}^{\cdot-}$ and O_2 as shown by Eq. 2-1 (Gierer et al., 1991; Sjöström, 1993).



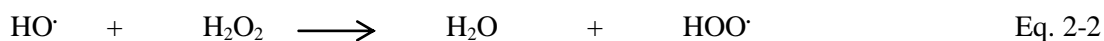
Scheme 2-1 The steps of oxygen reduction during O stage. I. The stepwise of reduction of oxygen in addition of one electron and proton to generate oxygen reactive species. II. The stepwise of generating organic radicals in O stage. (Sjöström, 1993; McDonough, 1996; Guay et al., 1999)



Amongst the oxygen reactive species, HO^\bullet is the most reactive species with redox potential $E^\circ \sim 2.7 \text{ V}$ and $E^\circ \sim 2.3 \text{ V}$ in acidic medium and neutral medium respectively (Gierer et al., 1991; Sjöström, 1993). As it has strong electrophilic nature, hence, it readily reacts with aromatic nuclei or double bond containing compounds in alkaline medium (Gierer et al., 1991). In addition, HO^\bullet can also undergo subtraction of hydrogen to form O^\bullet ($E^\circ \sim 1.4 \text{ V}$) in alkaline medium (Gierer et al., 1991; Sjöström, 1993). While, the redox potential for O_2^\bullet and HOO^\bullet is $E^\circ \sim 0.41 \text{ V}$ and $E^\circ \sim 0.81 \text{ V}$ correspondingly (Sjöström, 1993).

Johansson and Ljunggren (1993) claimed that an addition of a substantial amount of H_2O_2 may improve the effectiveness of O stage due to the formation of H_2O_2 decomposition constituents. As mentioned earlier, HO^\bullet is a highly reactive species in O stage and readily reacts with most of the organic substance especially hydrogen subtraction from H_2O_2 and HOO^\bullet (Eq. 2-2 and Eq. 2-3). By adding H_2O_2 , which is a weak acid ($pK_a = 11.8$), in O stage under a condition with $\text{pH} \approx 11.8$, the presence of H_2O_2 and its conjugated base (HOO^\bullet) is in almost equal amount. Since, HO^\bullet more readily reacts with HOO^\bullet than H_2O_2 under the

particular pH and/or higher pH condition, therefore, the reaction of Eq. 2-3 is faster than Eq. 2-2. This gives a good reason why carbohydrates are less degraded under higher pH condition as $O_2^{\cdot -}$ (the product of Eq. 2-3) is less reactive to carbohydrates. In contrast, under low pH condition, HO^{\cdot} tends to react with H_2O_2 because less HOO^{\cdot} is formed under the condition. This implies that only a relatively slower reaction between HO^{\cdot} and H_2O_2 occurs to form HOO^{\cdot} and water in low pH condition. Indirectly, this also indicates that more HO^{\cdot} retains in O stage system and it will react with lignin and carbohydrate non-selectively (Guay et al., 1999).



Despite that, the oxidation processes in an O stage system, as shown in Figure 2-1II are initiated by the reaction between the reactive substrates with O_2 and then form predecessor organic radicals (R^{\cdot} , RO_2^{\cdot}) (Eq. 2-4 and Eq. 2-5). While the reactive substrates, for example ionised free phenolic hydroxyl groups are activated under alkaline condition and/or the increased temperature of O stage. After the organic radicals are generated, the processes are then propagated and terminated as shown in Eq. 2-6, Eq. 2-7 and Eq. 2-8 respectively (Sjöström, 1993; McDonough, 1996).

Initiation:



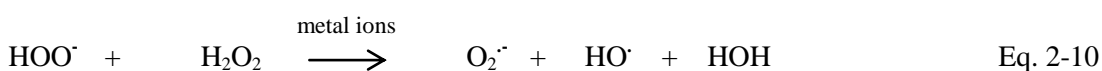
Propagation:



Termination:



The reactivity in O stage becomes more complicated with the presence of transition metal ions such as Fe^{2+} , Cu^{2+} , Mn^{2+} and Co^{2+} (Sjöström, 1993). The transition metals accelerate the decomposition of peroxide to $\text{HO}\cdot$ in O stage system as shown in Eq. 2-9 and Eq. 2-10. Due to the generation of high reactive and unselective $\text{HO}\cdot$ species, it may cause the carbohydrates to degrade severely (Sjöström, 1993; McDonough, 1996).



2.2.3.2 Reaction of Lignin in Oxygen Delignification

Lignin is the second abundantly available substance in lignocellulosic materials, which is amorphous and formed by inter-linkage of lignin units/monomers as shown in Figure 2-1 – syringyl (A), guaiacyl (B), veratryl (C), Me-syringyl (D) and etc (Sun et al. 1997). It is believed that 50 % and 60 % of the inter-linkage of lignin units in softwood and hardwood respectively are β -O-4 inter-unit linkages (Sjöström, 1993). The complexity of lignin in structure and its distribution in each part and species of plant are different. Therefore, instead of lignocellulosic materials, most of the studies on lignin reactivity have been done on lignin model compounds due to its usefulness to predict the lignin reaction in the pulping and bleaching process through the structural changes of lignin after pulping and bleaching. Since the changes of lignin structure may affect the reactivity of the following bleaching stage, to understand the structure of lignin after pulping and each stage of bleaching are very important in order to suit the best bleaching sequence to the pulp.

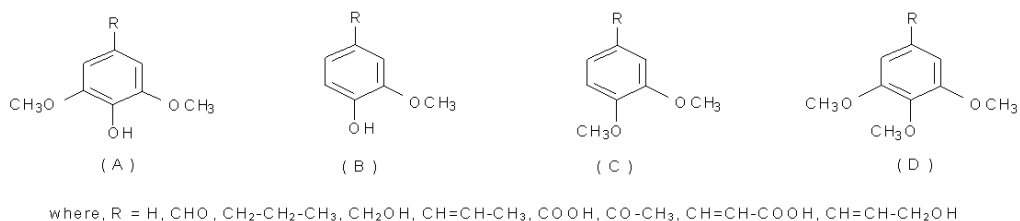
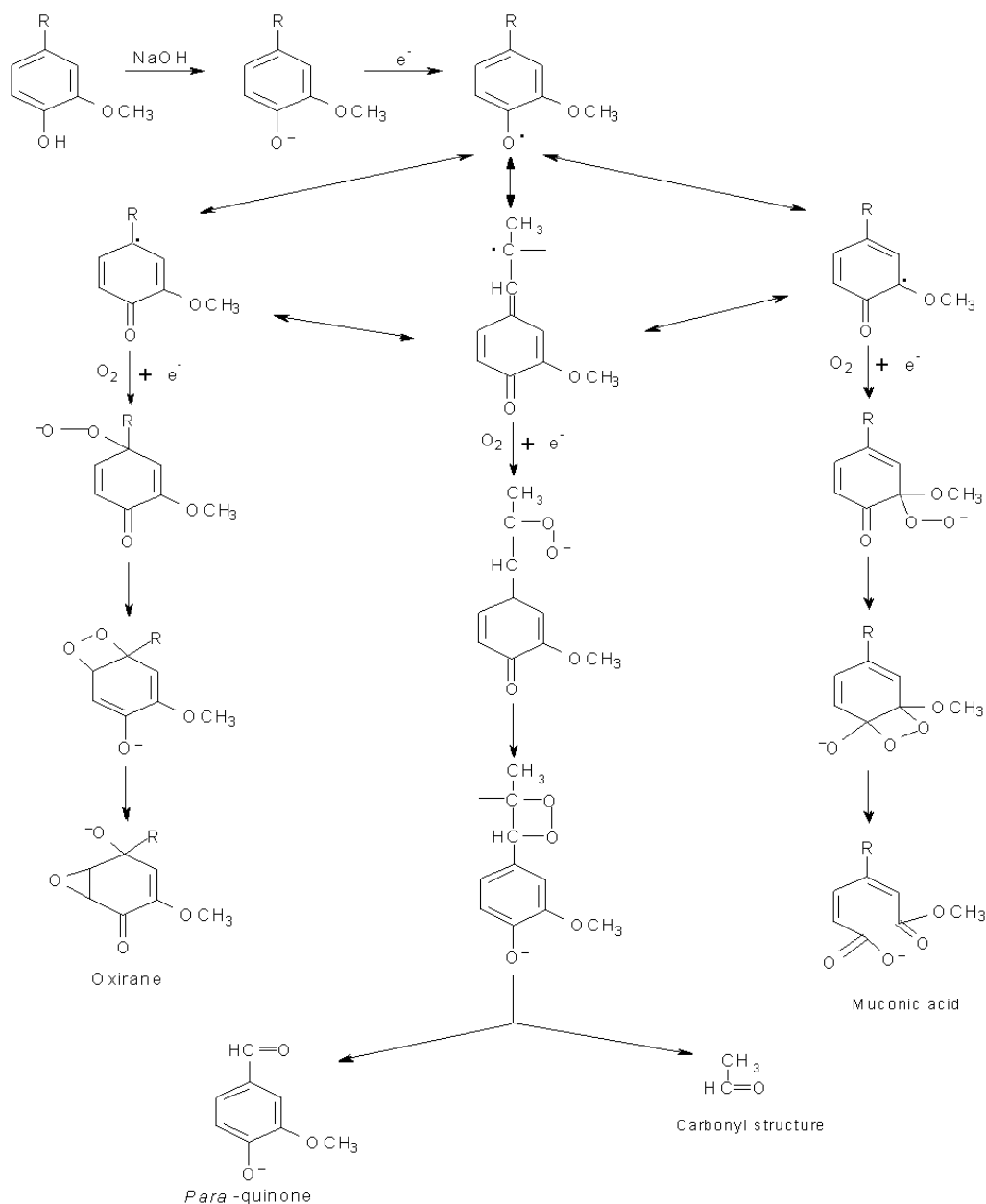


Figure 2-1 The bases of the lignin structure. (Sun et al., 1997)

In the bleaching process, there are two major feasible reactions which are electrophilic reaction (hydrogen abstraction, electron abstraction, and electrophilic addition) and nucleophilic reaction (nucleophilic addition, nucleophilic displacement, rearrangement, elimination of water and intramolecular nucleophilic addition). In comparison, electrophilic reaction is a more preferable reaction to delignify the pulp than nucleophilic reaction (Gierer, 1986; Sjöström, 1993; McDonough, 1996).

Similar to as other bleaching processes, O stage consists of both electrophilic and nucleophilic reaction. In O stage, the reactive species like HO[•], HOO[•] and O₂^{•-} act as electrophilic agent while HOO⁻ and HO⁻ as nucleophilic agent. Free phenolic groups in lignin structure are mainly reactive to the reactive species in O stage with the formation of phenoxyl radicals under alkaline condition. As shown in Scheme 2-2, electrophilic agents can attack the phenoxyl radicals to form a hydroperoxide intermediate followed by the formation of dioxetanes to induce the cleavage of the aromatic ring and side chain scission. Consequently, the oxirane, muconic acid (a type of carboxylic acid) and carbonyl structures are formed (Gierer, 1993 ; Sjöström, 1993; McDonough, 1996; Asgari and Argropoulos, 1998; Yang et al., 2003).



Scheme 2-2 Electrophilic reactions in O stage. (Gierer, 1993; Gierer et al., 1993; Asgari and Argyropoulos, 1998; Yang et al., 2003)

In addition, muconic acid and quinone are formed in O stage via nucleophilic agent with penoxy groups of lignin as shown in Scheme 2-3 (Sjöström, 1993; McDonough, 1996). The formation of muconic acid via nucleophilic reaction is almost the same as electrophilic reaction that hydroperoxide intermediate form followed by the formation dioxetanes to induce the cleavage of the aromatic ring.